

Chapter 3

Synopsis of Discussion Session: Influences of Particulate and Dissolved Material on the Bioavailability of Organic Compounds

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INTRODUCTION

The two basic routes of exposure by which organisms accumulate organic pollutants (bioavailability) are (1) transport across biological membranes exposed to the aqueous phase, and (2) direct ingestion of contaminated food particles. As our purview is to address the effects of particulate and dissolved material within the water and sediment environments on the bioavailability of organic chemicals, we will focus almost exclusively on how these materials influence the rate and magnitude of direct chemical transport across membranes from the external aqueous phase. Although contaminants associated with ingested food particles must cross biological membranes within the gut, digestive (catabolic) processes acting therein make this a unique route of exposure, separate from other routes in which membranes are in direct contact with the aqueous phase. In many instances, exposure via ingestion may contribute significantly to the overall uptake of a contaminant from the environment,^{1,2} although for most species its relative importance is poorly understood.

The role that sorption to organic or inorganic materials plays in controlling the bioavailability of ingested particle-associated contaminants is poorly understood. Additionally, while a discussion of mechanisms implies a discussion of mass transport from the source of the pollution, as well as the uptake kinetics and pharmacokinetics within the organism, we have emphasized the equilibrium relationships of these interactions and the conditions under which equilibrium assumptions may not be valid. A more thorough discussion of the kinetic aspects of bioavailability is the topic of another chapter.

The potential uptake of a chemical is influenced by the total concentration as well as the bioavailability of the chemical in the matrix in which the organism is exposed.³ Mass transfer processes such as bioturbation, resuspension, sedimentation, eddy currents, etc., will influence the environmental availability by altering the amount and/or environmental distribution of the chemicals. The environmental bioavailability of the contaminants to which organisms are exposed is affected by many factors, including association with solid and dissolved organic phases.⁴⁻⁹ Because it is the freely dissolved form of the contaminant which is transported across biological membranes, a reduction in the freely dissolved concentration (i.e., aqueous activity or fugacity) of the contaminant translates directly to reduced bioavailability. The characteristics of the solid or dissolved organic matter, as well as the chemical and physical properties of the contaminant, influence the mechanism and relative strength of the association. Therefore, an understanding of the mechanisms which control the sorption of organic chemicals to the solid and dissolved matrices is essential for understanding the magnitude of exposure as a function of environmental conditions.

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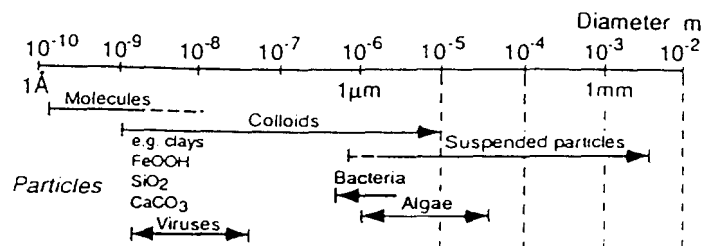


Figure 1. The size spectrum of waterborne particles. (From Stumm, W. and Morgan, J. J., *Aquatic Chemistry*, Wiley-Interscience, New York, 1981. With permission.)

FUNDAMENTAL AND EMPIRICAL RELATIONSHIPS

To predict the accumulation of organic pollutants transported across biological membranes, the freely dissolved concentration in the water column, $C_{w,aq}$, or the freely dissolved concentration in the pore water, $C_{s,aq}$, and the distribution of the organic pollutant among the various environmental phases ("compartments") in the system must be determined or predicted. Sediment-water systems are extremely heterogeneous, resulting in a wide variety of sorptive "sites" or phases within this complex assemblage of matrices. One classification scheme for these sorptive materials is based on size. Accordingly, materials range in size from simple dissolved molecules, to complex dissolved material (macromolecules), to colloids, to large suspended particles, to bedded sediment aggregates of organic and inorganic material (Figure 1). The heterogeneous particles will have different capacities for the same organic pollutant, resulting in different sorptive phases on the same particle. For example, Weber et al.¹⁰ have shown that distributed sorption by sediment does occur.

Equilibrium Partitioning

The aqueous concentration, C_{aq} , at equilibrium is related to the distribution coefficients, K_i of the various phases (i) according to the mass balance equation:

$$\frac{C_{aq}}{C_T} = \frac{1}{1 + \sum K_i f_i} \quad (1)$$

where, f_i is the mass of each phase (kilograms) per volume of water (liters) in the system, and C_T is the total concentration in the system, normalized to the aqueous phase volume. Although there is a continuum of possible size fractions of the sorptive phases, three fractions have been described most by researchers: dissolved organic matter (DOM) (measured as dissolved organic carbon, DOC), suspended solids (SS), and bulk sediments (SED). The definitions of these materials as sorptive "fractions" or "phases" are operational, and designations for the different sizes of the fractions are a matter of convention. For example, DOM is often defined as that material which passes through a 0.45- μm filter, which includes both truly dissolved organic species and some colloidal material. Estimating C_{aq} depends on the accurate measurement of K_i and f_i values for each phase. It must be remembered that it is not necessary to base the summation term on only one bulk property of each size fraction (e.g., the organic carbon content); several types of sorptive sites may exist within each size fraction (e.g., clay minerals, organics, oxides). Heterogeneous particles will contain regions of differing affinity within each individual particle for the same organic pollutant.^{10,11}

The sediment-water system can be represented by a high solids content sediment layer and a low solids content water layer, separated by a phase boundary (Figure 2); although the boundary is never so distinct in most natural systems. Each layer contains analogous components of water,

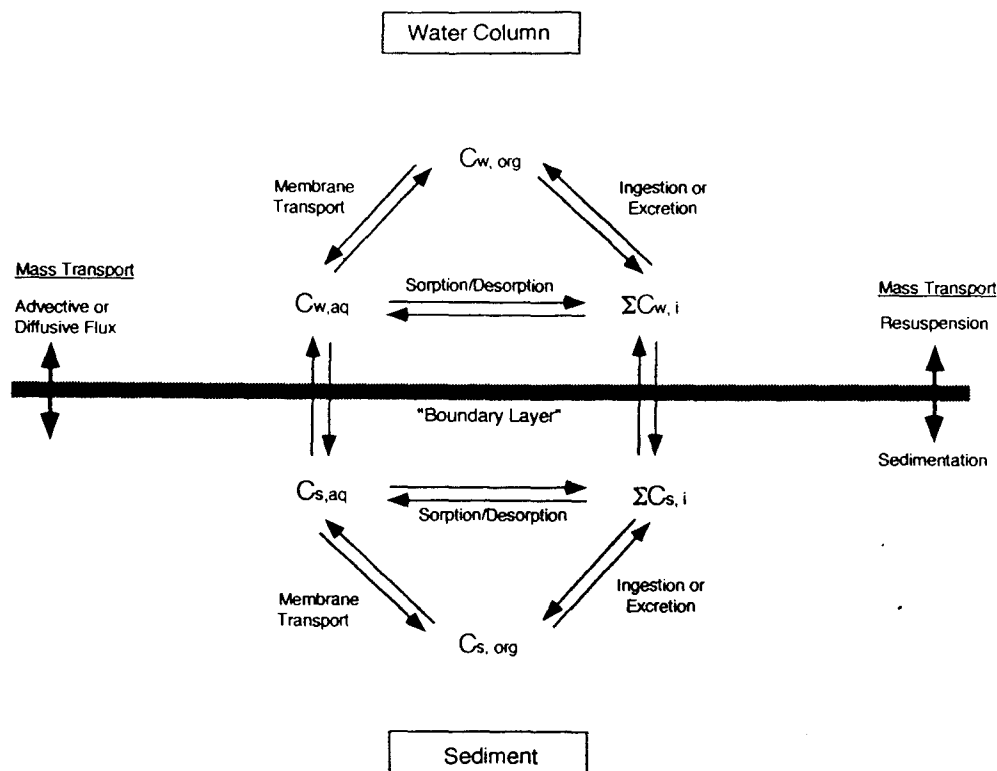


Figure 2. An equilibrium partitioning approach to the distribution of organic pollutants in water-sediment systems. The first subscript indicates the environmental compartment (w = water, s = sediment) and the second subscript refers to the phase within that compartment, e.g., aq = aqueous (freely dissolved), org = organism (biota), and i = any pollutant sorbing phase (e.g., bulk sediment, suspended sediment, colloids, DOM).

biota, and a plethora of nonliving sorptive phases. Exchange is relatively rapid among components in the “water layer”, but intrasediment and water-sediment exchange may be much slower. Therefore, equilibrium cannot be assumed across the sediment-water boundary.¹² Furthermore, the quantity and nature of sorbents in the sediment layer will differ from those in the water column above, so that $C_{w,aq}$ is not necessarily equal to $C_{s,aq}$ for the same mass of chemical and the same solids mass/water volume ratio. As a result, Equation 1 should be applied separately to the two “layers” if the equilibrium assumption is made.

Figure 2 shows the partitioning of an organic pollutant within and between two multiphase systems—one on each side of the sediment-water interface. The associated contaminant concentrations are $C_{w,aq}$, $C_{w,org}$, and $\Sigma C_{w,i}$, or $C_{s,aq}$, $C_{s,org}$, and $\Sigma C_{s,i}$, assuming the interactions are at steady-state or equilibrium in the water column and sediment domains, respectively.^{4,13–17} $C_{w,org}$ and $C_{s,org}$ are the pollutant concentrations associated with the biota of the aqueous and sediment layers, respectively. $C_{w,i}$ and $C_{s,i}$ are the contaminant concentrations in each of the sorbing phases, i , of the water column (e.g., suspended sediments) and bulk sediment environments, respectively. Figure 3 shows the simplest case approximation of two homogeneous sorbing phases in each layer, $\Sigma C_{w,i} = \{C_{w,ss} + C_{w,doc}\}$ and $\Sigma C_{s,i} = \{C_{s,ss} + C_{s,doc}\}$, where $C_{w,ss}$, $C_{s,ss}$, $C_{w,doc}$, and $C_{s,doc}$ are the contaminant concentration in the suspended sediment, bulk sediment, water column DOM, and pore water DOM phases, respectively. Since natural surface waters usually contain significant DOM (1 to 30 mg/l),¹⁸ it is always necessary to include $C_{w,doc}$ and $C_{s,doc}$ terms in the $\Sigma C_{w,i}$ and $\Sigma C_{s,i}$ sums, respectively. Thus, the physical nature of the water column is best described by, at

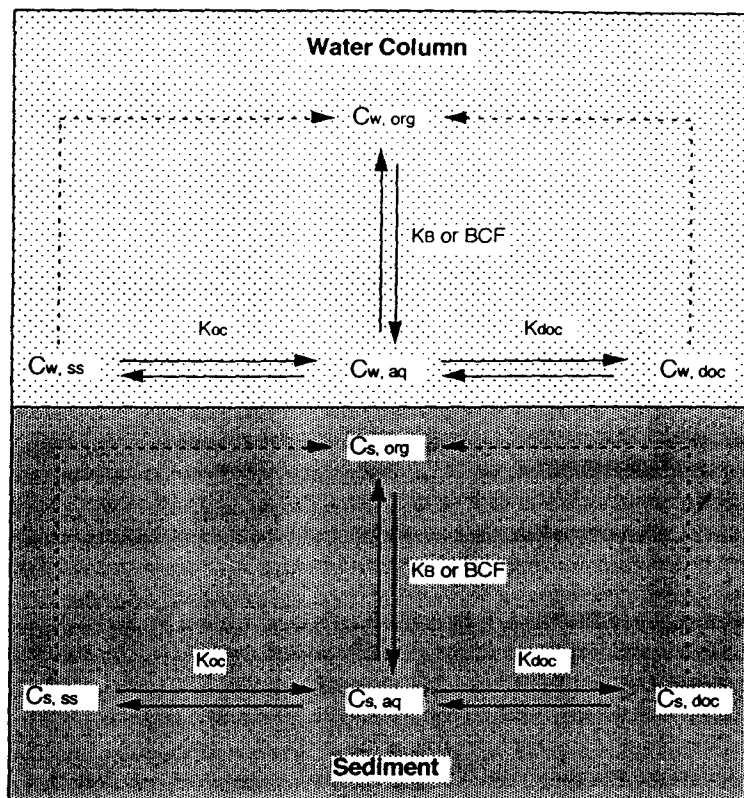


Figure 3. A simple four-phase model describing the bioavailability of organic pollutants in aquatic systems. The freely dissolved fractions of the contaminant ($C_{w,aq}$ and $C_{s,aq}$) are the most bioavailable. However, the contribution from bound fractions ($C_{w,ss}$, $C_{w,doc}$, $C_{s,ss}$, and $C_{s,doc}$), indicated by the dashed lines, may become important for certain organisms via ingestion as part of the food supply.

minimum, a three-phase system consisting of water, suspended solids ($>0.45 \mu\text{m}$), and dissolved organic matter (soluble and colloidal fraction $<0.45 \mu\text{m}$).^{3,4,6,13-15,17}

Although only the freely dissolved phases are bioavailable via external biological membranes, at thermodynamic equilibrium the final concentration of the chemical in the organism is independent of the route by which the organism is exposed to the chemical.¹⁹ This results from the fact that, at equilibrium, the chemical potentials (or fugacities) in all phases (SED, SS, DOM, water, and biota) are equal. As stated previously, however, catabolic reactions in the gut may render ingested particle or DOM-associated contaminants bioavailable (hence the dashed lines in Figure 3).

The sediment-water partition coefficient (K_{sed}) can be normalized to the organic carbon content of the sediment,

$$K_{oc} = \frac{K_{sed}}{f_{oc}} = \frac{C_{s,ss}}{[(C_{s,aq} + C_{s,doc}) \times (f_{oc})]} \quad (2)$$

where f_{oc} is the mass fraction of organic carbon in the sediment expressed as a decimal. Spacie²⁰ describes the factors affecting solid-phase equilibrium conditions. Organic carbon-based partitioning in sediments (i.e., partitioning described by K_{oc}), is presently the best general approach to define the interactions between the sediments and organic pollutants with octanol-water partition coefficients (K_{ow}) greater than 2 (Table 1). The use of the organic carbon normalized partition

Table 1. Compounds of Interest for the Study of Bioavailability in Water

Nonpolar Organics	Examples
$\log K_{ow} > 5$	Polychlorinated biphenyls Perylene <i>p,p'</i> -DDT
$2 < \log K_{ow} < 5$	Lindane Anthracene Atrazine
$\log K_{ow} < 2$	Toluene Methylene chloride Acetone
Polar Organics	Examples
Organic acids	2,4-D Chlorophenols Nitrophenols
Organic bases	Acridine Aniline Quinoline

coefficient, K_{oc} , has been shown to successfully predict the freely dissolved species concentrations to within better than a factor of 10 when the f_{oc} is greater than 0.003 (i.e., sediment OC > 0.3%).²¹

Experimental evidence elucidating the mechanisms that affect local microenvironmental conditions in the sediment is limited. These conditions, which include mineral matrix effects and the chemical structure of the organic matter, affect sorption capacity (i.e., fugacity capacity). Variability in the nature and properties of organic carbon increase the uncertainty in the prediction of C_{aq} from K_{oc} . It may be possible to improve upon our present predictive capability by increasing our understanding of the chemical characteristics and binding properties of different forms of organic carbon. For example, the K_{oc} term in Equation 2 might be subdivided according to size fractions or functional classes of humic material.

The K_{oc} partitioning approach is also applicable to organic matter-pollutant interactions in the water column or pore water (e.g., colloids and suspended sediment). However, the predictive ability of this approach modified for the DOC phase commonly varies by more than a factor of 10.^{5,22,23} Some of this variation can be explained by the molecular characteristics of the DOM such as aromaticity, molecular size distribution, or hydrophobic acid content,^{6,22,24} as well as water quality conditions (e.g., oxic vs. anoxic conditions).²⁵ It is evident that accurate prediction of the water column aqueous activity will require an understanding of the extent to which different classes of organic chemicals partition to the various fractions and forms of the DOM.

As previously stated, equilibrium is achieved when the free energy, chemical potential, or fugacity of a chemical in all environmental compartments (i.e., sediment, DOM, water, and biota) are equal. If a chemical exhibits equivalent partitioning behavior toward lipid and organic carbon, then at equilibrium the organic carbon normalized concentration (C_{oc}) of the chemical will be the same as the lipid normalized organism concentration, $C_{s,org}$ or $C_{w,org}$, for sediment-dwelling or water-column organisms, respectively. Experimentally measured partition coefficients for organism lipid and sediment organic carbon generally agree within an order of magnitude.¹⁹ Some of this variation can be explained by the molecular characteristics of DOM such as aromaticity, molecular size distribution, or hydrophobic acid content.^{26,27} For many nonionic organic compounds this could be extended, and the K_{ow} used to predict K_{oc} and the bioconcentration factor (K_B or $BCF = C_{biota}/C_{water}$). The simplest approach is to assume that $K_{ow} = K_{oc} =$ lipid normalized K_B (BCF), or that organic carbon, lipid, and octanol are all equivalent in terms of partitioning. More accurate predictions of K_B requires recognition that the above assumption is not valid, and that these parameters are

generally related by $K_B = F_1(K_{oc}) = F_2(K_{ow})$, where F_1 and F_2 are empirically determined mathematical functions.²⁸

Sorption to Bulk Sediment

DiToro et al.²⁹ have recently reviewed the available information related to bioavailability of nonionic organic contaminants in bulk sediment under near-equilibrium conditions. They conclude that there is essentially no relationship between sediment chemical concentrations (total dry weight basis) and biological effects. However, the chemical concentrations in the pore water ($C_{s,aq}$), or the sediment chemical concentrations on an organic carbon normalized basis at which biological effects occur, vary only by a factor of around 2 for most sediments and chemicals. Furthermore, the observed biological effects concentration determined in water-only exposures is the same as those predicted or measured in sediments.²⁹ Similarly, DeWitt et al.²¹ found that K_{oc} values were able to predict free concentrations of fluoranthene within better than a factor of 10 when the f_{oc} is greater than 0.003 (0.3%). Hence, organic carbon normalized partitioning is presently the best general approach to estimate near-equilibrium interactions between the sediments and nonpolar, nonionic organic pollutants with K_{ow} greater than 2 to 3. This applies to suspended sediments in the water column as well as the pore water environment of superficial sediments.

Sorption to Colloidal and Dissolved Material

Unlike K_{oc} 's of bedded or suspended sediments, the organic carbon normalized partition coefficient, K_{oc} 's, of a given pollutant to natural DOM varies among the waters from different sources.^{4,13,14,22,30-34} The affinity of DOM for sorption of organic pollutants has been related to various chemical properties of DOM. In a series of studies,^{6,22,35} the aromaticity of DOM in natural water was found to correlate to the observed binding capacities. In other studies, the polarity of the DOM fraction^{25,36-38} and molecular size^{36,37} were found to correlate to the binding capacities.

Kukkonen et al.²⁴ have shown differences in binding capacities of benzo(a)pyrene (BaP) and polychlorinated biphenyls (PCB) congeners for three XAD-8 resin DOM fractions of differing polarity from one natural source (Figure 4). Most importantly, it was also shown that the carbon-normalized binding coefficients, K_{oc} 's, of these chemicals in the original water can be calculated as a sum of the relative K_{oc} 's of the three fractions. In addition to the differences in binding among the different fractions, it was shown that BaP is bound to both of the operationally defined hydrophobic fractions (neutral and acidic), while the affinity of PCB was mainly to the hydrophobic neutral fraction.²⁴ It is also possible to explain earlier observed differences in K_{oc} values for compounds with similar K_{ow} values (PAHs vs. PCBs), through differences in binding to the different DOM fractions, and the resulting apparent solubility enhancement.

DOM can also be fractionated by apparent molecular weight (for example, by ultrafiltration) in order to investigate the binding capacities of the resulting fractions. It has been shown that in oxic waters, the larger molecules and colloids have the highest binding capacities.^{25,36-38} This phenomenon is illustrated in Table 2, which shows that when removing the greater than 100,000 Dalton (Da) fraction from water (about 10% of total DOC), about 45% of the binding capacity of DOM is removed.³⁸ However, Hunchak-Kariouk²⁵ has recently shown that in anoxic sediments this may not hold true. In a study of the binding of 2,2',4,4'-tetrachlorobiphenyl with DOC under anoxic conditions (i.e., $E_h < -350$ mV), the smaller molecular weight fraction (<5000 Da) exhibited the highest binding capacity. However, when the anoxic water was aerated to an oxic condition (i.e., $E_h > +200$ mV), the higher molecular weight fraction (>5000 Da) once again had the highest binding capacity. In a subsequent study, Hunchak-Kariouk and Suffet³⁹ observed that the $K_{s,doc}$ (sediment water-DOC partition coefficient) is a more sensitive function of DOC

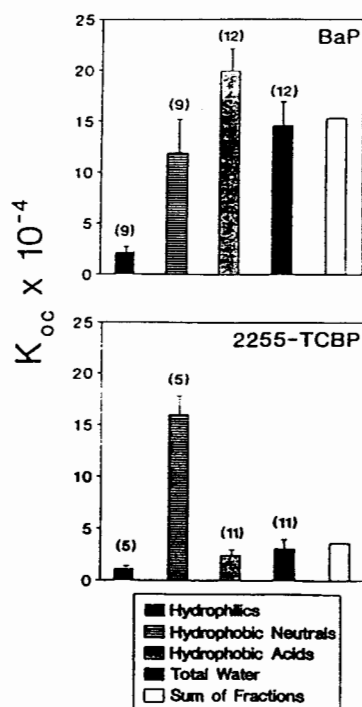


Figure 4. The K_{oc} of benzo(a)pyrene (BaP) and 2,2',5,5'-tetrachlorobiphenyl (2255-TCBP) to DOM fractions and total unfractionated water. Mean \pm SD and (n) are shown on charts. (From Kukkonen, J., McCarthy, J. F., and Oikari, A., *Arch. Environ. Contam. Toxicol.*, 19, 551-557, 1990. With permission.)

Table 2. Partition Coefficients (K_{oc} ; Mean \pm SD, n = 6) of Benzo(a)pyrene to Different Molecular Size Fractions of DOM Obtained by Ultrafiltration

MW Fraction	DOC (mg/l)	% of total DOC	K_{oc}
Filtered (0.45 μ m) unfractionated water	49.9	100.0	$1.34 \pm 1.5 \times 10^5$
<100,000 Dalton	44.6	89.4	$7.2 \pm 2.0 \times 10^4$
< 30,000 Dalton	34.9	69.9	$3.1 \pm 1.0 \times 10^4$
< 10,000 Dalton	24.8	47.5	$0.5 \pm 0.2 \times 10^4$
< 5,000 Dalton	17.2	34.5	$< 10^3$
< 1,000 Dalton	5.0	10.0	$< 10^3$
< 500 Dalton	1.7	3.4	not analyzed

Note: Water source: Hyde County, NC, U.S.

From Kukkonen, J., *Effects of Dissolved Organic Material in Fresh Waters on the Binding and Bioavailability of Organic Pollutants*, University of Joensuu, Finland, 1991. With permission.

concentration in anoxic as compared to oxic conditions (Figure 5). Therefore, to understand the actual environment under study, samples must be maintained oxic or anoxic after sampling and throughout analysis.

If the partitioning of the chemical to lipid is the same as to the solid or dissolved organic carbon, at equilibrium the organic carbon normalized contaminant concentration (micrograms per kilogram of carbon) will be approximately the same as the lipid normalized contaminant concentration (micrograms per kilogram of lipid) in the organism. Indeed, Bierman¹⁹ has shown that for a range of organisms (both benthic and pelagic) and log K_{ow} 4 to 8, partition coefficients for organism lipid and sediment organic carbon often agree within an order of magnitude. Because a direct measure of the chemical activity in the water is not required, this approach would be a

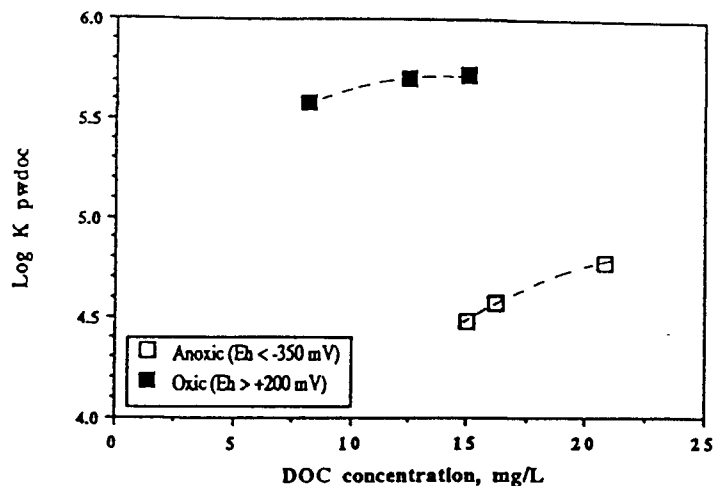


Figure 5. Influence of DOC concentration on the calculated K_{pwdoc} (i.e., $K_{a,doc}$ herein) values for oxic and anoxic pore waters extracted from the same sediment sample. (From Hunchak-Kariouk, K. and Suffet, I. H., *Finn. Humus News*, 3, 157–170, 1991. With permission.)

Table 3. Analytical Methods Used in Determining the Association of Organic Chemicals to Dissolved Organic Matter

Physical Separation Methods	Solubility Enhancement Measurements
<ul style="list-style-type: none"> • Liquid-liquid extraction • Equilibrium dialysis • Reverse-phase chromatography • Ultrafiltration • Molecular size exclusion chromatography 	<ul style="list-style-type: none"> • Apparent water solubility • Fluorescence quenching • Headspace-free equilibration

very useful and practical tool for predicting the bioavailability of nonionic organic chemicals in sediments. For sediments, the equilibrium assumption appears to apply for a wide variety of chemicals and sediment types.²⁹ However, this assumption does not seem to apply as well to DOM in sediment pore water^{13,17} and in the water column.^{4,14,22,30–34}

METHODS OF DETERMINING AQUEOUS CONCENTRATION IN THE PRESENCE OF DISSOLVED ORGANIC MATTER

When an appreciable amount of DOM is present in the water, estimation of C_{aq} for very hydrophobic chemicals ($\log K_{ow} > 5$) is problematic. Several approaches have been introduced to determine the freely dissolved concentration or activity of such chemicals in the aqueous phase (Table 3). All of the methods described to date have limitations to their universal application, especially for estimations or calculations in natural environments. The most desirable technique is one that avoids the operational definitions of the phase or fraction and measures the aqueous activity directly. A summary of these methods is provided below, along with their major limitations:

- In liquid-liquid extraction procedures,^{40–42} the freely dissolved pollutant is extracted from equilibrated solution with solvent. The extraction procedure, however, may be so efficient that weak pollutant-DOM interactions are broken and the amount of freely dissolved pollutants is overestimated.
- In equilibrium dialysis,³⁰ the DOM sample is closed within a dialysis bag and immersed in pollutant containing DOM-free water. The technique is limited to pollutants that can pass through the dialysis

membrane and DOM that cannot escape from the dialysis bag (normal molecular cut off, 1000 Da). Time is required to reach equilibrium, and mass balances must be performed to account for any binding to the dialysis membrane.

- The reverse-phase separation method⁵ requires passage of an equilibrated solution of DOM and a pollutant through a sorbent (C-18) column that selectively retains only the freely dissolved pollutant. However, this process alters the equilibrium in the solution, which may result in some DOM-bound pollutant desorption. This method may lead to underestimating the K_{oc} value. On the other hand, if the freely dissolved compound does not adsorb totally to the column some breakthrough could result and K_{oc} could be overestimated. Also, small particles or colloids, possibly present in the water, can be retained by the column and the portion of the compound bound by these will be miscalculated as freely dissolved and this will result in underestimating the K_{oc} value.
- In ultrafiltration,⁴³ an equilibrated solution of DOM and pollutant is subjected to molecular size separation, so that the freely dissolved pollutant is filtered through a membrane and sorbed pollutant is retained with the DOM. The technique requires special equipment and is limited to compounds which should not interact with ultrafiltration membranes.
- In size exclusion chromatography,⁴² molecular size separation occurs in a molecular sieve chromatography column where freely dissolved and DOM-bound pollutant fractions are separated. This method is limited to compounds that do not interact with the resin or are not partly retained by the resin. Some of the same limitations of the reverse-phase separation methods apply.
- The apparent water solubility enhancement resulting from the presence of organic matter can be used to estimate the K_{oc} , and therefore the freely dissolved concentration, by discrete solubility measurements⁴⁴ or generation columns.¹³ Carefully removing the pure solid or liquid phase chemical from the system is the key to success of both these methods. Colloidal particles of low density could be included in the solubility measurement.
- Fluorescence quenching methods³⁵ are based on the observation that molecules that normally fluoresce do not fluoresce when bound to DOM. The technique is limited to those compounds that fluoresce and to only well-defined waters (i.e., one compound) where interfering fluorescence is not a problem.
- Headspace methods are based on chemicals coming into equilibrium air above or passed through the solution containing the chemical of interest. Only the freely dissolved chemical is available for transfer across the air-water interface, and therefore the concentration of the free chemical in the water can be calculated from the air concentration and the Henry's Law constant of the chemical. For compounds with a low Henry's Law constant, the concentration of the chemical in a static air phase at equilibrium is near or below the analytical detection limits. Therefore, this method has been adapted to a dynamic system which essentially allows for larger headspace volume and the concentration of the chemical to meet analytical requirements.^{42,45} Organic films formed at the air-water interface may influence the mass transfer, particularly in natural waters. Aerosols may also be included as part of the air phase concentration, resulting in overestimation of the freely dissolved concentration.

A four-phase system, including solid phase, DOM, freely dissolved chemical, and biota, has been used to describe the partitioning of organic contaminants in both water and sediment (Figure 3). While normalizing DOM partition coefficients to the organic carbon content may be inappropriate in many instances, such is not the case for partition coefficients of neutral organic compounds to the solid sediment phase. The significance of this for the approximation of the general environmental distribution of literally thousands of organic chemicals can not be overestimated.

Operationally, definitions of the phases has led to errors in the measurement and interpretation of K_{oc} values. Direct or indirect measurements of the chemical concentrations in the solid, DOM, and freely dissolved phases are required to avoid artifacts associated with estimating these values in both the laboratory and field. For some compounds, complete extraction and quantification of compound associated with the organic matter requires exhaustive extraction or digestion.⁴⁶ Methods which measure the aqueous activity directly, such as headspace analysis and fluorescence methods, also avoid operational definitions of the phases and need to be more thoroughly developed and evaluated for routine use. The measurement of the freely dissolved concentration of the

chemical has been, and continues to be, a major problem associated with determination of accurate K_i values (e.g., K_{oc} for organics), as well as the ability to quantitatively judge whether equilibrium has been attained.

In summary, methods used to determine the value of K_i generally involve the measurement or estimation of: (1) the fraction of the medium responsible for the observed distribution (e.g., organic carbon), (2) the concentration of the chemical associated with each of these fractions or phases, and (3) the freely dissolved concentration (i.e., activity). There are methodological limitations to the determination of each of these values. Failure to adequately separate the phases, or accurately measure the concentration the chemical in each of the phases at equilibrium, can lead to significant errors in the determination of the K_i (e.g., K_{oc}) values. Therefore, improved methodologies are required for characterizing partition coefficients, particularly among aqueous-phase components such as DOM, where K_{oc} values appear to be inappropriate as predictive tools. At present, it is not clear what to measure to predict K values for the continuum that is DOM.

Humic Substances

A considerable amount of the solid, colloidal, and dissolved organic material in natural environments consists of diagenetic carbon, otherwise known as humic substances. The term humic substances refers to organic material in the environment that results from the decomposition of plant and animal residues, but which does not fall into any of the discrete classes of compounds such as proteins, polysaccharides, and polynucleotides. Humic substances are an extraordinarily complex mixture of compounds.⁴⁷ Humic acids, that fraction of humic substances which are insoluble in water at $\text{pH} < \sim 2$, differ from fulvic acids (soluble under all pH conditions) in elemental and functional group compositions, average molecular weights, and other characteristics.⁴⁸ The major functional groups in humic substances are carboxyl, phenolic hydroxyl, and alcoholic hydroxyl. Typical average molecular weights of fulvic acids are 800 to 1000 Da, whereas those of humic acids are 2000 to 3000 Da. Materials with a greater oxygen content will have a greater concentration of functional groups. This composition is likely to cause the material to be more hydrophilic, and consequently less effective in the complexing (binding) of hydrophobic nonionic organic compounds.

Humic substances do not occur alone in the environment. Rather, they are mixed with, or chemically or physically associated with, other classes of materials. Most researchers isolate the humic substances from the nonhumic materials and independently evaluate the characteristics and behavior of the isolated materials. Other researchers have used the total humic-water solution itself, and characterized it. Of these approaches, the latter is best in that it more closely approximates reality.

The average concentration of the humic substances in the surface waters is 2.2 mg of carbon per liter or 4.4 mg of humic substances per liter.¹⁸ Humic substances are approximately 50% carbon (DOC) by weight. Although the DOC of colored surface waters is extremely variable, it typically ranges from about 5 mg/l to more than 50 mg/l. Also, in these colored waters the fraction of the total DOC composed of humic substances varies considerably, and can be as large as 80%.⁴⁹

In summary, an understanding of the influences of humic materials is only sufficient to define site-specific effects on the pollutants. As information is accumulated, it is hoped that a more general understanding of the effects of humic substances on organic pollutants will be developed to help predict effects in unknown situations. It is recommended that the study of the molecular structure of humic material, especially these so-called water-soluble fractions, be further characterized when studies on the humic-organic interaction are performed. As a minimum, oxic-anoxic integrity, size fractionation, separation by lipophilicity, and determination of aromaticity should be considered in experimental design. Improved methodologies are required for characterizing partition coefficients, particularly among aqueous phase components.

The Solids Effect

Based on the assumption of linear two-phase equilibrium sorption, K_i in Equation 1 should be constant with increasing or decreasing suspended sediment concentrations, where K_i is simply the K_{oc} of the suspended sediment solid phase. However, numerous authors have demonstrated that there is a decline in the measured values of the apparent partition coefficient, K_p , when the suspended sediment concentration is increased.^{16,50,51} This phenomenon is the well-known “solids effect”. This inconsistency led DiToro⁵² and Mackay and Powers⁵³ to hypothesize a particle-induced desorption of chemical from suspended sediments, which intensifies as the suspended sediment concentration increases. An alternative hypothesis suggested by several investigators^{14–16} attributes the decrease in K_p to a methodological artifact. They suggested that inadequate separation of the phases and sorption of the chemical to an unaccounted-for third phase, colloids, or DOM, results in the overestimation of the aqueous concentration. Recent studies, which have attempted to use methods to directly measure the free dissolved concentration utilizing headspace techniques, have reduced or eliminated the solids concentration effect.²³ The observed effect can also be the result of kinetic effects when there is failure of the system to reach equilibrium before concentration measurements are made. Clearly, the time frame for approach to equilibrium is dependent on the rate of molecular diffusion of the specific chemical in water and the sorbing material, the partition coefficient(s), and the diffusional path length(s) within the sorbing material.

In summary, there is sufficient experimental evidence to conclude that the solids concentration effect is an experimental artifact and can be attributed to the influence of DOM, colloids, and/or kinetic factors (e.g., intraaggregate diffusion). The multiphase equilibrium model which includes DOM, sediment, freely dissolved phase, and kinetic considerations can provide an explanation of the artifact. In addition, for systems with high sediment concentrations, kinetic models may be important tools for assessing whether the equilibrium assumption is valid.

Ionizable Organic Compounds

The rather simplistic categorization of chemicals due to their hydrophobicity (e.g., K_{ow}) to describe their interactions with sedimentary and dissolved material is often inappropriate. Many chemicals contain polar functional groups which interact specifically with distinct sorption sites or may modulate sorption due to nonspecific hydrophobic interactions.⁵⁴ In any case, the magnitude of the interactions of these compounds, even with sedimentary solids, is often not well predicted based on the carbon content of the sediment. Two clear examples were given in Session 4, Chapter 1 by Spacie²⁰—simple organic acids, and simple organic bases. Instead of a linear combination of sorption processes as expressed in Equation 1, the partitioning of these compounds must be expressed as a $2 \times n$ matrix of species (neutral or ionic) distributed to n sorptive phases. That is, the distribution of these compounds can be modeled as a linear combination of independent partitioning reactions of the neutral and ionic forms. Partitioning of the neutral form generally can be assumed to obey the same general trends presented above for strictly neutral compounds. The distribution of the ionic species, however, is strongly affected by electrostatic interactions; the significance of each species-specific interaction is controlled by the magnitude of these interactions, as well as by the difference between the pH of the system and the pK_a of the ionizable compound.

Some general observations, however, can be made. For organic acid compounds, the neutral form generally partitions to sedimentary material to a greater extent than the corresponding anion. In fact, significant sorption of the anionic form generally does not occur unless the aqueous pH is at least 2 units above the pK_a . Below this range (i.e., $pH < pK_a + 2$), the distribution can be estimated by simultaneous solution of the equations for acid dissociation, partitioning of the neutral species, and the mass balance equation on total compound in the system.⁵⁵ When the $pH > pK_a + 2$, partitioning of the organic anion cannot be neglected; however, good predictive

methodologies do not exist for estimating this effect. This same effect is observed in the distribution of these compounds in both octanol-water systems⁵⁶ and in the bioavailability of these species across the gill.⁵⁷ In both octanol-water and sediment-water systems, the distribution of the anion is effected by the ionic composition of the media.

In contrast to the anionic species, the cationic form of organic bases generally associates to sedimentary materials to a greater extent than the corresponding neutral form. These compounds can associate with sediment components through hydrophobic or modified hydrophobic mechanisms, cation and/or ligand exchange type reactions, or chemical reactions leading to the formation of covalent bonds through nucleophilic addition or oxidative processes. Similar to the organic acids, differentiation among these processes is necessary to estimate the amount of material that is bioavailable under near steady-state or perturbed environmental conditions.⁵⁸

In summary, the partitioning behavior of nonionized forms of organic acids and bases is similar to nonpolar neutral organics, as would be expected. Organic anions generally sorb less than their nonionized form, whereas organic cations generally sorb more strongly than their corresponding nonionized form. For the organic acids with low pK_a , generally K_p is very low (e.g., less than 10^3), and sorption to bed sediments may be the only significant interaction with natural materials. Currently, no methodologies exist for predicting sorption of organic bases. Clearly, a better understanding of factors controlling partitioning of organic acids and bases is necessary.

Mass Transport Processes

A more quantitative interpretation of Figures 2 and 3 can be made by examining the relative magnitudes and rates of transfer for various organic compounds. As was previously stated, the significance of mass transfer limitations between phases and compartments is affected by the characteristics of the specific compound of interest. The high molecular weight PCBs and PAHs are prime examples of compounds that partition extensively to biota, DOM, and sediment solids. This distribution, while limiting the total amount of material that may be bioavailable to organisms, is also important in limiting chemical and biological degradation reactions in the environment, as discussed by Crosby.⁵⁹ In general, it is the compounds such as those mentioned above, with organic carbon normalized partition coefficients, K_{oc} , greater than 10^5 , for which association with dissolved or colloidal material may be important both in the laboratory and in the field (Table 1). Thus, in the summation terms in the denominator of Equation 1, $K_{DOM} f_{DOM}$ is a significant fraction of 1 or greater than 1. While f_{DOM} (kilograms per liter) is small for nonsettleable solids or dissolved materials, the corresponding K_{DOM} is large. Obviously, in sediments, partitioning of these compounds to both the material in the interstitial water and to the solid matrix is important.

While the capacity of bedded sediments as a sink or a source of contamination is great, and the total exchangeable mass of these contaminants may be large, there is usually an extremely low gradient of mass transfer between this compartment (the sediment layer) and the water column as equilibrium is approached.¹² The relative rate of this exchange compared to other transport processes into and out of the control volume (water and sediment layer), results in at best a steady-state diffusional approximation of the environmental distribution of the chemical, and hence a steady-state approximation of the bioavailability of the contaminant, as these fluxes change with conditions. Therefore, water-layer organisms are more often not at equilibrium with sediment-layer contaminants.

For those compounds with log K_{ow} values between 2 and 5, that is, moderately hydrophobic compounds (Table 1), association with nonsettleable solids or dissolved materials is generally insignificant in comparison to the association with bedded sediments, as the product of $K_{DOM} f_{DOM}$ is less than 1. In bedded sediments, the total mass of the solid phase per volume water, f_{sed} , is large, and significant amounts of these compound may be associated with this material. Because of the moderate hydrophobicity of these compounds, this association is generally well correlated

to the organic carbon content of the sediment layer (for neutral nonpolar compounds, specifically). Therefore, the denominator of Equation 1 can be approximately expressed as $(1 + K_{oc}f_{oc})$, where K_{oc} is the organic carbon normalized partition coefficient, and f_{oc} is the mass of organic carbon in the sediment per water volume.⁶⁰ For the more hydrophobic compounds, similar calculations are valid for the solid matrix, however, in these systems diffusional processes generally limit attainment of equilibrium. This often results in layered contamination, where relatively clean recent and older sediments are separated by a layer of contaminated sediments. In boreal peat bogs, this layering effect is often evident because of the low turnover or scour potential of the system. Essentially, instead of two compartments (water and sediments), slow contaminant fluxes between several sediment compartments may limit transport, and hence, bioavailability. Similar conditions may often exist in the water column, where transport is limited by mixing barriers such as a thermocline or a salt wedge. While lake turnover events disrupt this effect in the water column, this effect is disrupted at the water-sediment interface by natural changes in hydraulic scour (due to sedimentation itself, for example), storm events, dredging, and bioturbation.

Many environmentally significant compounds display weak association to natural materials. These compounds may be small nonhydrogen-bonding compounds such as benzene, methylene chloride, or mono- or dichloroethanes; hydrogen-bonding polar compounds such as nitrobenzene or bis(2-chloroethyl)ether; or ionizable compounds such as phenols and cresols, or even the phenoxyacetic acid herbicides which are essentially completely ionized at neutral pH (pK_a of ~ 3 to 4). While sorption of these compounds may be very significant in bedded sediments or soils present in agricultural runoff, a quantitative estimation of their environmental distribution is somewhat problematic. This may become even more significant as more polar compounds replace hydrophobic compounds as pesticides and for other uses, since it is their discharge that requires regulation. At present, very little is known regarding their mass transfer rates in the environment.

Physiological and behavioral characteristics of biota may contribute to the nonequilibrium distribution of chemical between the biota and the other phases. Organism growth and metabolic transformations may prevent the chemical concentration in the organism from approaching equilibrium with the surrounding medium (water and/or sediment). Tropic transfer may cause the chemical activity in the organism to exceed that in the water (bioconcentration).² Benthic organisms may have widely different levels of exposure because of selectivity in the size and nature of the particles they ingest.⁶¹

In summary, future studies are needed to define mass transfer from the solid phase to the pore water, and mass transport from the pore water to the overlying water column. Moreover, studies that test hypotheses of processes controlling mass transport at specific sites should be conducted in order to have a better understanding of the relative importance of specific physical, chemical, and biological mechanisms, and to develop better predictive tools (i.e., models).

CONCLUSIONS

1. The most appropriate measure of the bioavailable fraction of an organic chemical is the aqueous activity. This applies to the water column as well as the pore water environment of superficial sediments.
2. Organic carbon normalized partitioning is presently the best general approach to estimate the short-term interactions between the sediments and nonpolar organic pollutants with $\log K_{ow}$ greater than 2.
3. Partitioning to dissolved organic matter (DOM) generally correlates poorly with the organic carbon content of the DOM, as variations in K_{oc} for DOM exceed a factor of 10. These constants are conditional and site specific, as local water quality may determine the character, and hence, the binding properties of the DOM. For optimization of the analysis system, maintenance of water quality is suggested (e.g., oxic/anoxic conditions, pH, ionic strength, etc.).

4. Improved methodologies are required for characterizing partition coefficients, particularly among aqueous phase components. At present, it is not clear what to measure in order to predict K_{oc} for the continuum of material that is DOM. Characterization of the operationally defined dissolved organic carbon (DOC) phase—those organic materials that pass through a 0.45- μm filter—should be performed when studying bioavailability, particularly when the $\log K_{ow}$ of the compound of interest is greater than 5. Suggestions for characterization include size fractionation, lipophilicity, and aromaticity.
5. Observed variations in partition coefficients with solids concentration, the so-called “solids effect”, can be explained by a combination of kinetic effects and artifacts in the measurement of the aqueous activity.
6. A better understanding of mass transfer processes between the soluble phases ($C_{w,aq}$ or $C_{s,aq}$) and the solid phases ($C_{w,i}$ and $C_{s,i}$), is needed for better predictions of bioavailability. Bioconcentration and bioaccumulation of organic contaminants is a dynamic process.
7. A better understanding of the relative importance of various uptake routes for benthic organisms is necessary. The exact role that sorption to organic or inorganic materials plays in controlling bioavailability via ingestion is poorly understood and requires future study.
8. A better understanding of factors controlling the association of organic acids and bases to soluble and solid organic phases is necessary.

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